



Catalyst-selective, scalable membraneless alkaline direct formate fuel cells



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ABSTRACT

We present here a membraneless alkaline direct formate fuel cell (DFFC) with a catalyst-selective strategy, in which a non-hazardous, inexpensive alkaline aqueous formate solution is used as an anolyte. The novel catalyst-selective strategy not only avoids the use of practically unviable alkaline anion-exchange membranes, but also overcomes the scalability limitation of the traditional membraneless DLFCs that are based on a micro-flow phenomenon, and allows the development of large-scale membraneless DLFCs with flexible configurations. In comparison to methanol, ethanol, and formic acid fuels, the aqueous formate solutions show superior oxidation kinetics and efficiency. The high power density exhibited by the membraneless alkaline DFFC is promising for developing small, safe, inexpensive portable power systems as well as large-scale energy generation systems.

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1. Introduction

Among the various types of fuel cells, the proton exchange membrane fuel cells (PEMFCs) are in the forefront owing to their advantageous features, especially being operable at low temperatures. H_2 -fed PEMFCs and PEM-based direct liquid fuel cells (DLFCs) are the dominant options to be considered as promising power sources for portable, automobile, and stationary applications [1–3]. In comparison to the H_2 -PEMFCs, liquid-fed fuel cells possess obvious advantages in terms of fuel storage, transportation, safety, and simple cell configuration. Among the PEM-based DLFCs that are at different stages of development, the direct methanol fuel cells (DMFC), direct ethanol fuel cells (DEFC), and direct formic acid fuel cells (DFAFC) have attracted particular attention [4–8]. However, despite many years of intensive research into these DLFC technologies, inherent limitations still remain to be overcome.

Under the PEMFC operation conditions, the kinetics of oxygen reduction reaction (ORR) in a weakly acidic environment is considerably slow. The large overpotential for the ORR has been a major issue with PEM-based fuel cells as it constitutes a large

portion of the total-cell voltage loss [9–11]. In contrast, the ORR kinetics in alkaline medium is facile, therefore, alkaline DMFCs and DEFCs based on anion-exchange membranes (AEM) have recently attracted much attention [12,13]. However, the AEM technology is not yet reliable enough for the alkaline fuel cell development and implementation in terms of efficiency, stability, and cost.

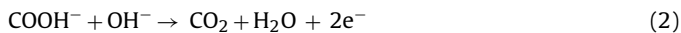
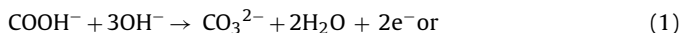
In addition to the sluggish ORR kinetics with PEMs and the lack of a viable AEM, both the DMFC and DEFC technologies are facing other challenges: (i) the high rate of methanol or ethanol fuel crossover from the anode to the cathode through the membrane reduces the fuel utilization and decreases the cell performance, limiting the concentrations of the fuels used in practical cells [14,15]; (ii) both the methanol and ethanol oxidation reaction kinetics are also slow, necessitating high loading of expensive catalysts [16,17]; and (iii) the inherent toxicity of methanol also is an issue [18].

In comparison to the DMFC and DEFC, DFAFC utilizing formic acid as a fuel offers the advantages of facile oxidation kinetics of formic acid fuel, high theoretical cell voltage, and low fuel crossover [19]. However, since a DFAFC has to be operated in acidic medium, the slow ORR kinetics in acidic medium is a formidable challenge. Use of formates, e.g., sodium or potassium formate, as fuels is expected to operate the DFAFC analogous to the fuel cells in alkaline medium. Actually, the formate $HCOO^-$ has been speculated as a poisoning species to deactivate the anode catalysts in DFAFCs, which might have limited the use of formates as anode fuels. A recent mechanistic study has realized that the deactivation of the anode catalysts is not relevant to the adsorption of formate species

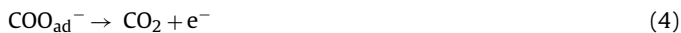
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[20]. Actually, formate has been proved to be readily oxidized on Pd catalysts in alkaline media as indicated below [21–24].



From a fundamental point of view, formate oxidation reaction (FOR) on Pd/C electrode is generally considered to follow a mechanism in accordance with the reactions (3)–(5) below [24,25].



This mechanism is important since there is no surface CO poisoning issue during the FOR on Pd. Oxidation of adsorbed COO^- and desorption of hydrogen each contributes one-electron charge transfer. The above information has recently generated interest to develop alkaline direct format fuel cells (DFFCs) since 2012 [26–29]. However, like other alkaline DLFCs, although the DFFC can be demonstrated with an AEM, further development of this technology is inevitably limited by the lack of industrially viable anion-exchange membranes.

We present here a membraneless alkaline DFFC that avoids the above obstacles. The membraneless strategy is inspired by an experimental observation that the highly ORR active cathode catalyst (Pt) does not have catalytic activity for the formate oxidation reaction (FOR). Therefore, crossover of the fuel to the cathode is not a serious issue, and the alkaline anion-exchange membrane can be excluded from the cell. Proper management of the anode/cathode catalysts also provides the feasibility for the development of large-scale membraneless direct liquid fuel cells without scalability and configuration limitations.

2. Experimental

2.1. Preparation of anolytes and electrolytes

Potassium formate and sodium formate from Alfa Aesar® were dissolved in, respectively, 1.0 M KOH and 1.0 M NaOH solutions to form different concentration anolytes/electrolytes. Methanol and ethanol from Fisher scientific® were added into 1.0 M KOH solution to form the aqueous alkaline electrolyte. Formic acid from Alfa Aesar® was added into 1.0 M H_2SO_4 to form the aqueous acidic electrolyte.

2.2. Preparation of electrodes

Catalysts employed in this study include 40% Pd/C (40 wt. % Pd on Vulcan® XC-72, E-TEK), 40% Pt/C (40 wt. % Pt on Vulcan® XC-72, E-TEK) and 40% PtRu/C (40 wt. % Pt-Ru (Pt:Ru = 1:1) on Vulcan® XC-72, E-TEK). The catalyst was dispersed in a mixture of de-ionized (DI) water and a certain volume of Nafion solution (5%, DuPont®) by sonication for 10 min. The mass ratio of net Nafion to the catalyst was 1:4 (mass ratio) in all cases. The resulting ink was deposited onto a carbon fiber paper (Toray HP-60) and dried in air for 1 h at room temperature.

2.3. Three-electrode electrochemical experiments

Cyclic voltammetry and linear sweep voltammetry experiments were conducted in a conventional three-electrode glass cell with a Pt mesh counter electrode. Hg/HgO and Hg/Hg₂SO₄ reference electrodes were used, respectively, in the alkaline and acidic electrolytes. The working electrodes were prepared by depositing 1.6 mg of the catalyst (including carbon support and Nafion) onto

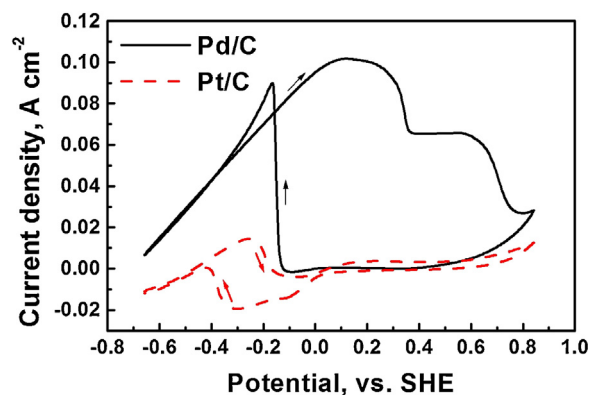


Fig. 1. Cyclic voltammograms of Pd/C and Pt/C electrodes in an electrolyte containing 1.0 M HCOOK in 1.0 M KOH at 20 mV s^{-1} . Experiments were performed at ambient temperature.

a 1.0 cm^2 area of a strip of carbon fiber paper. The electrochemical data were collected with a potentiostat (VoltaLab PGZ 402, Radiometer Analytical).

2.4. Fuel cell performance testing

An in-house designed membraneless alkaline DFFC with 5.0 cm^2 active area was used for cell performance test. Details of this cell will be described in Section 3.3. The operation of the membraneless alkaline DFFC was controlled with a fuel cell test station (850E, Scribner Associates Inc.).

3. Results

3.1. Selective oxidation reaction of formate on Pd/C and Pt/C in alkaline media

Fig. 1 shows the cyclic voltammetry (CV) profiles of Pd/C (0.5 mg cm^{-2} Pd) and Pt/C (0.5 mg cm^{-2} Pt) electrodes in an electrolyte containing 1.0 M HCOOK in 1.0 M KOH. As seen in Fig. 1, the oxidation current of HCOOK on Pd/C electrode increases almost linearly in the potential range of -0.7 to 0.1 V (vs. SHE), which is a matched potential domain for the alkaline fuel cell operation. The voltammetric behavior of the carbon-supported palladium (Pd/C) electrode here agrees with the mechanism of the formate oxidation reaction (FOR) on pure Pd catalyst under similar conditions [22–24]. However, it is difficult to discern the oxidation currents of the FOR from those caused by the hydrogen desorption, presumably due to the unique mechanism for the FOR on Pd in alkaline media as described in Eqs. (3)–(5). On the other hand, the oxidation current at potentials greater than 0.1 V (vs. SHE) does not make sense in an alkaline fuel cell (the cell voltage will be less than 0.3 V since the ORR potential in alkaline medium is 0.4 V (vs. SHE)), so the voltammetric behavior above 0.1 V in Fig. 1 will not be discussed in this paper.

However, from Fig. 1, it is surprising to see that Pt/C does not provide any significant catalytic activity for the oxidation of potassium formate. The FOR current on the Pt/C electrode is almost negligible in contrast to that generated on the Pd/C electrode. Actually, FOR on the Pt-based catalyst has not yet been well understood, since the mechanistic study regarding FOR on Pt surface has scarcely been reported (presumably, such a study is less attractive to researchers due to the less active behavior of Pt for FOR). A recent study preliminarily proposed that formation of CO intermediates and the presence of other possible inhibitory processes (such as OH adsorption) prevent the oxidation of formate on Pt surface [30].

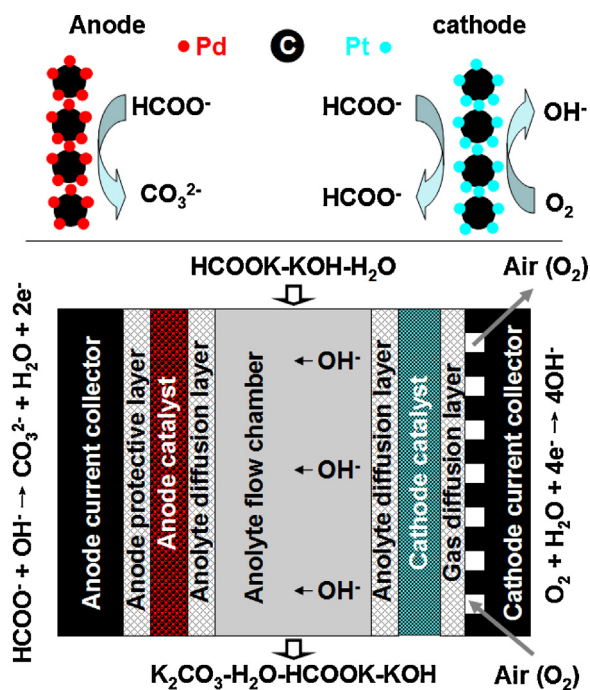


Fig. 2. Schematic of a membraneless alkaline direct formate fuel cell (DFFC) and the selective oxidation of formate on the catalysts.

3.2. Concept of the catalyst-selective membraneless DFFC

The cyclic voltammetry profile of Pt/C electrode shown in Fig. 1 along with the 'inhibitory mechanism [30]' of FOR on Pt seems to provide a negative information for researchers since Pt is by no means a favorable catalyst for FOR in alkaline medium. However, such an observation is particularly useful. From a full cell point of view, the above 'disappointing' information provides a possibility to develop a 'membraneless' DFFC, as illustrated in Fig. 2.

In this in-house designed fuel cell, Pd/C and Pt/C were, respectively, used as anode and cathode catalysts. An aqueous solution comprising HCOOK as fuel and KOH as supporting electrolyte was fed as an anolyte through a chamber between the anode and the cathode catalyst layers. In traditional alkaline liquid-fed fuel cells, the role of an alkaline anion-exchange membrane is to provide a conductive path for the OH^- ion migration and to prevent the crossover of the liquid fuel and the oxidants. In the fuel cell shown in Fig. 2, the supporting electrolyte KOH sustains the migration of OH^- ions. Since the cathode catalyst Pt does not catalyze the anode reaction, oxidation of potassium formate will not take place at the cathode. In addition, fairly low solubility and diffusivity of oxygen in an aqueous alkaline solution suggests that the crossover of the cathode oxidant is not an issue either [31,32]. Therefore, the anion-exchange membrane used in the traditional alkaline DLFCs appears to be not necessary in this fuel cell.

It should be noted in Fig. 2 that in order to prevent the anolyte flow washout to the catalyst, two anolyte diffusion layers made of carbon fiber paper were applied to each side of the cell between the catalyst layers and the anolyte flow. Furthermore, two pieces of carbon fiber paper were additionally placed to each side of the cell between the catalyst layers and the current collectors. The one at the cathode serves as a gas diffusion layer, and the other at the anode is used to protect the anode catalyst.

3.3. Validation of the membraneless DFFC

The membraneless DFFC was validated with the operation of a cell with 5 cm^2 active electrodes (areas of the anode and the cathode

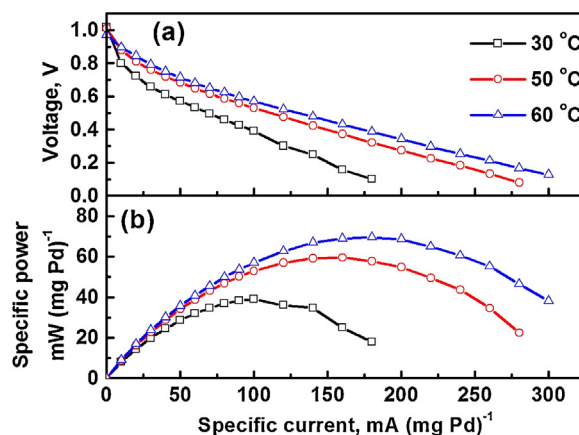


Fig. 3. Performance of the membraneless alkaline direct formate fuel cell operated at various temperatures. (a) Polarization curves and (b) power plots.

are identical) and a 2 mm thick flow chamber, as shown in Fig. 2. For the single cell measurements, an anolyte solution containing 2.0 M HCOOK in 2.0 M KOH was pumped through the flow chamber at a flow rate of 0.5 mL min^{-1} . Oxygen was fed to the cathode at a flow rate of 100 mL min^{-1} , and the back pressure was maintained at 30 psi. The Pd loading at the anode and the Pt loading at the cathode were both 1.0 mg cm^{-2} . Cell performances were tested at various temperatures of 30, 50, and $60\text{ }^\circ\text{C}$.

Fig. 3 shows the polarization curves and the corresponding power plots of the membraneless DFFC operated at different temperatures. As seen in Fig. 3, the open-circuit voltage of the membraneless DFFC is ca. 1.1 V, which is higher than those of DMFC, DEFC, and DFAFC. Since the reliable Pt catalyst with a sufficient loading was used in this cell, the cathode reaction would not limit the performance of this cell. The specific current and specific power of the membraneless DFFC was then normalized based on the anode catalyst (Pd) loading. Under the testing conditions demonstrated in this study at $60\text{ }^\circ\text{C}$, the specific power of the membraneless DFFC is ca. $75\text{ mW (mg Pd)}^{-1}$ and the specific current at 0.6 V is ca. $100\text{ mA (mg Pd)}^{-1}$. Since the main purpose of this study is to validate the concept, catalyst loading was not optimized. The performance shown here is comparable to the DFFCs with an alkaline anion-exchange membrane [26–29] and those of alkaline direct alcohol fuel cells under the same catalyst loading [33,34].

In this study, Pd/C was used at the anode since Pd is known as the most powerful and stable catalyst for formate oxidation reaction so far. In comparison to Pt, Pd is less expensive (only 1/5 of the price of Pt). However, use of Pt/C as the cathode catalyst in this study is just to validate the concept as it is a reliable catalyst. Since the cathode reaction proceeds more rapidly in alkaline media, the ORR catalysts in the alkaline DLFCs are expected to be less demanding. Actually, quite a lot of research is progressing on non-noble metal catalysts for ORR in alkaline medium. For example, alkaline DEFCs have been demonstrated recently with non-precious metal catalysts [35,36]. Thus, the development of membraneless DFFCs will not have to rely on the expensive Pt cathode catalyst. Alternate, less expensive catalysts can be developed.

3.4. Half-cell comparison of formates with other liquid fuels

Among the low-temperature direct liquid fuel cells, DMFC, DEFC, and DFAFC have been mostly emphasized and are being in different stages of development. In this study, we compared the anode reaction kinetics of the formates with those of methanol, ethanol, and formic acid. In order to avoid the influence from the full cell operation conditions, oxidation kinetics of the liquid fuels was compared with electrochemical experiments conducted in a

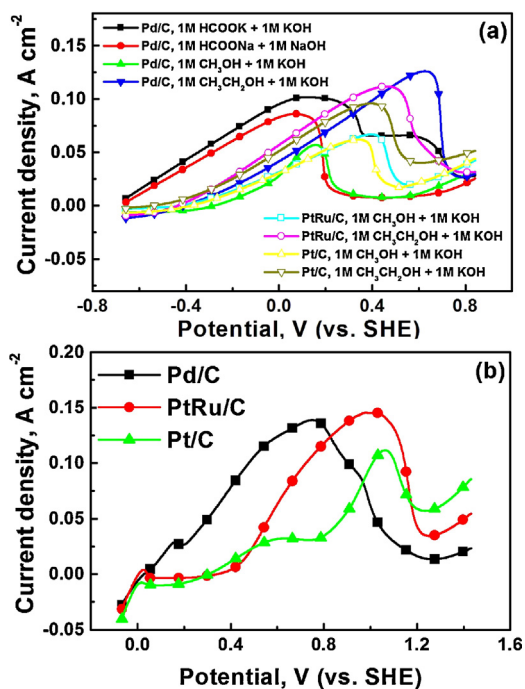


Fig. 4. Linear sweep voltammograms of Pd/C, PtRu/C, and Pt/C electrodes in various alkaline and acidic electrolytes. (a) Alkaline electrolytes of 1.0 M HCOOK + 1.0 M KOH, 1.0 M HCOONa + 1.0 M NaOH, 1.0 M CH₃OH + 1.0 M KOH and 1.0 M CH₃CH₂OH + 1.0 M KOH and (b) acidic electrolyte of 1.0 M HCOOH + 1.0 M H₂SO₄. The scan rate is 20 mV s⁻¹. Experiments were performed at ambient temperature.

three-compartment electrochemical cell. The concentration of each fuel was maintained at 1.0 M (methanol, ethanol, potassium formate, sodium formate, and formic acid). 1.0 M KOH or 1.0 M NaOH were used as supporting electrolytes for methanol, ethanol, potassium formate, and sodium formate, while 1.0 M H₂SO₄ was used as the supporting electrolyte for formic acid. The electrodes were prepared with the best catalyst (with the same loading of 0.5 mg cm⁻²) as known for the oxidation of each fuel. PtRu/C and Pt/C catalysts were used for the study of methanol and ethanol, while Pd/C was used for the study of potassium formate, sodium formate, and formic acid. The average particle sizes of the Pt/C, PtRu/C, and Pd/C catalysts are almost the same (~2–4 nm), so the active surface area of the catalysts used for this comparison is similar as well.

Fig. 4(a) and (b) show the linear sweep voltammetry profiles of PtRu/C, Pt/C, and Pd/C electrodes in 1.0 M CH₃OH + 1.0 M KOH, 1.0 M CH₃CH₂OH + 1.0 M KOH, 1.0 M HCOOK + 1.0 M KOH, 1.0 M HCOONa + 1.0 M NaOH, and 1.0 M HCOOH + 1.0 M H₂SO₄ electrolytes. As seen in Fig. 4(a), in comparison to methanol and ethanol, potassium formate and sodium formate are oxidized much more efficiently and at lower potentials. Throughout the potential domain, which is consistent with the fuel cell operation (–0.7 to 0.1 V vs. SHE), the oxidation rates of the two formates are significantly higher than those of methanol and ethanol. For the oxidation of formic acid, Pd/C shows the highest activity (Fig. 4(b)) as expected.

Oxidation rates of the two formates and the formic acid are not directly comparable from the voltammetry profiles shown in Fig. 4(a) and (b), since DFFC and DFAFC are, respectively, operated in alkaline and acidic media. To make a direct comparison and learn the oxidation kinetics of the formates and formic acid fuels at the identical fuel cell operating voltages, their voltammetry profiles are plotted by subtracting their oxidation potentials from the ORR potentials in acidic (1.23 V vs. SHE) and alkaline (0.40 V vs. SHE) media (Fig. 5a).

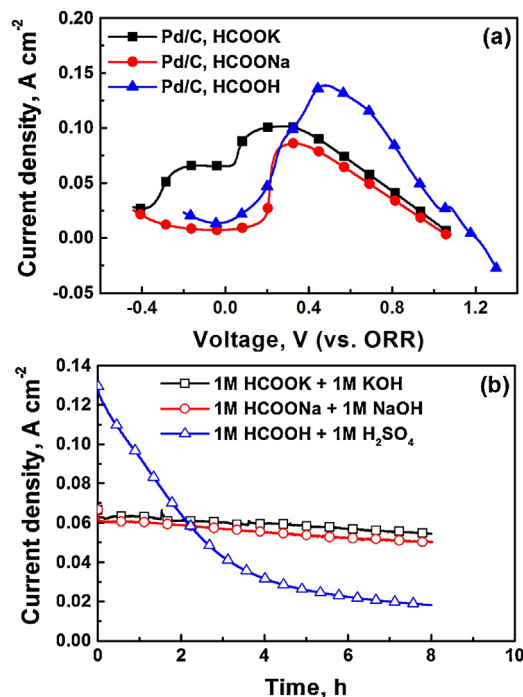


Fig. 5. Comparison of the oxidation kinetics between formates (in alkaline medium) and formic acid (in acidic media). (a) Linear sweep voltammograms plotted by subtracting the oxidation potentials from the standard oxygen reduction potentials in different media (0.40 V in alkaline medium, 1.23 V in acidic medium) for a Pd/C electrode in the electrolytes of 1.0 M HCOOK + 1.0 M KOH, 1.0 M HCOONa + 1.0 M NaOH, and 1.0 M HCOOH + 1.0 M H₂SO₄. (b) Current vs. time curves for a Pd/C electrode in the electrolytes of 1.0 M HCOOK + 1.0 M KOH, 1.0 M HCOONa + 1.0 M NaOH, and 1.0 M HCOOH + 1.0 M H₂SO₄. Experiments were performed at fixed potentials of –0.25 V (vs. SHE) for the formate fuels and 0.58 V (vs. SHE) for the formic acid fuel, which correspond to an identical 0.65 V fuel cell operation voltage in all cases (standard oxygen reduction potentials are 0.40 V in alkaline media and 1.23 V in acidic media). The experiments were performed at ambient temperature.

The results in Fig. 5(a) indicate that formic acid is more readily oxidized on the Pd/C catalyst in acidic media than its counterpart formates in alkaline media. However, due to the inherent ‘dual pathway’ mechanism of the electro-oxidation of formic acid, the oxidation rate is not stable under DFAFC conditions which has always been a main issue for the DFAFC development [37]. Fig. 5(b) compares the long-term oxidation rates of potassium formate, sodium formate, and formic acid on Pd/C catalyst at a fixed fuel cell operation voltage of 0.65 V (vs. ORR potentials in alkaline and acidic media, respectively). Although the initial oxidation currents for sodium formate and potassium formate are lower than that for formic acid, their currents are stable. Consequently, the oxidation currents of the two formates exceed that of formic acid after ca. 2 h of continuous operation. In consideration of the activity and durability, the formate salts show superior practical oxidation characteristics than the other liquid fuels including methanol, ethanol, and formic acid that are commonly used for the DLFCs development.

4. Discussion

Like the formic acid, oxidation reaction of the formate salts theoretically involves 2-electron charge transfer (see Eqs. (1) and (2)), which is lower than those involved with the oxidation reactions of methanol (6-electron) and ethanol (12-electron). However, from the comparison results above (Figs. 4 and 5), the oxidation kinetics and efficiencies of the formates are superior to those of other liquid fuels including methanol and ethanol as well as the formic acid. From the thermodynamic point of view, the open-circuit potential

of a DFFC is about 1.45 V (as calculated from the Gibbs free energy change of a full cell reaction) [26]. Therefore, the DFFCs have a higher electromotive force (EMF) than either DMFCs (OCV = 1.21 V) or DEFCs (OCV = 1.14 V) [27]. Based on the superior oxidation kinetics of the formate fuel and the high electromotive force of the fuel cell reaction, the DFFC system is able to generate higher practical energy than the other direct liquid fuel cells.

Under alkaline conditions, facile electrode reactions can be assessed in a DFFC with less expensive anode and cathode catalysts. Our ongoing work includes validation of such cells with non-noble metal catalysts, with various fuels and maximization of the power densities. Exclusion of the membrane not only avoids the need for inefficient and costly anion-exchange membranes, but also simplifies the cell configuration and lowers the cell component cost. Actually, at the current stage, transition of the traditional lab-scale 'proof of concept' membraneless fuel cells into commercially viable micro-fluidic power generation system is still challenging. Since the traditional membraneless fuel cells are usually based on a micro-flow phenomenon and rely on maintaining a laminar flow regime, scale-up of such fuel cells is not technically feasible [38]. In this regard, the catalyst-selective strategy demonstrated in this study is a 'game changer'. It enables membraneless direct liquid fuel cells to be built in any scales and with flexible configurations.

From the fuel cell operation point of view, formate salts are non-hazardous and can be easily handled as stable solids or in aqueous solutions. The formate solutions in alkaline media are not volatile below the water boiling point (100 °C), which is an additional advantage compared to methanol, ethanol, and formic acid. Furthermore, the products of formate salts can be obtained from renewable sources via artificial photosynthesis and are inexpensive. In addition, as illustrated in Fig. 2, the reaction products of DFFCs are only carbonate and water. Therefore, the DFFC systems provide a safe, low-cost, and environmentally benign process for energy conversion.

5. Conclusions

Use of the catalyst selectivity strategy provides a new pathway strategically to develop membraneless direct liquid fuel cells. This novel strategy not only avoids the need for expensive proton-exchange membranes and/or reliable alkaline anion-exchange membranes, but also provides the important advantages of scalability of DLFCs with more flexibility in the cell-configuration design. Its implementation will be simpler than membraneless fuel cells that depend on non-mixing laminar flows. In this study, we demonstrated such a catalyst-selective, membraneless strategy with an alkaline DFFC system. Facile electrode reactions, including both the electro-oxidation of formate and the electroreduction of oxygen, could be realized in such a cell. The aqueous formate solutions show oxidation kinetics superior to that of other liquid

fuels. The membraneless alkaline DFFC system has the potential for addressing the rapidly growing need for low-cost, large-scale energy generation and high-energy density portable power systems.

Acknowledgement

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